

Final Project Report

Localized Corrosion Analysis Laboratory
Defense University Research Instrumentation Program
for FY 1998 and 1999

Program contract no. F49620-98-1-0251

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June, 2000



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REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-00-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project Director (0304-0188), Washington, DC 20503.

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 2000		3. REPORT TYPE AND DATES COVERED Final - 1 March 1998 - 30 September 1998	
4. TITLE AND SUBTITLE Localized Corrosion Analysis Laboratory				5. FUNDING NUMBERS F49620-98-1-0251	
6. AUTHOR(S) Rudolph G. Buchheit Materials Science and Engineering					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Ohio State University Columbus, OH 43210				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 North Randolph Street Arlington, VA 22203-1977				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The funds were used to construct the Localized Corrosion Analysis Laboratory in the Fontana Corrosion Center to study corrosion across all relevant length scales. This laboratory comprises a scanning probe microscopy stations specifically designed for corrosion and electrochemistry, an novel electrochemical microprobe, a rotating ring-disk collections system, a multiplexed electrochemical workstation, a novel multichannel (100 channel) microelectrode array system, a constant extension rate test system, and an alternate immersion exposure chamber.					
14. SUBJECT TERMS Corrosion, electrochemical				15. NUMBER OF PAGES 9	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclass	18. SECURITY CLASSIFICATION OF THIS PAGE Unclass	19. SECURITY CLASSIFICATION OF ABSTRACT Unclass	20. LIMITATION OF ABSTRACT		

Project Summary

This report describes facility instrumentation purchased by the Fontana Corrosion Center at Ohio State University between March 1, 1998 through September 30, 1999 under the AFOSR/DURI Program contract no. F49620-98-1-0251 entitled "Localized Corrosion Analysis Laboratory". The AFOSR award of \$150,975 was matched with \$75,488 from the Ohio Board of Regents and \$75,487 from The Ohio State University Office of Research, College of Engineering, and Department of Materials Science and Engineering bringing the total available funding for this facility to \$301,950. Funds were fully committed by 9/30/99 and fully expended by 11/30/99 and the project is now closed to further procurement.

The funds were used to construct the Localized Corrosion Analysis Laboratory in the Fontana Corrosion Center to study corrosion across all relevant length scales. This laboratory comprises a scanning probe microscopy station specifically designed for corrosion and electrochemistry, an novel electrochemical microprobe, a rotating ring-disk collection system, a multiplexed electrochemical workstation, a novel multichannel (100 channel) microelectrode array system, a constant extension rate test system, and an alternate immersion exposure chamber. The components of this laboratory are explained in more detail in this report.

Electrochemical Microprobe

The electrochemical microprobe unites optical microscopy with electrochemical corrosion measurements. The microprobe is shown in Figure 1. The system consists of a glass microcapillary cell mounted on the carousel of an Olympus BX60M optical microscope, video camera and external monitor, and a high current resolution Autolab PGSTAT-100 potentiostat capable of 30 fA current resolution. The system software permits the full suite of DC electrochemical measurements to be made.

The optical microscope is placed in a Faraday cage for noise control. We use this system to make spatially resolved electrochemical measurements on very heterogeneous microstructures. The capillary cell can be drawn down to a diameter of 1 to 10 μm if necessary, and probe placement can be made within a few micrometers. We use this system to make measurements on heterogeneous Al alloy surfaces and to make measurements on specially synthesized ingots containing intermetallic compounds.

The primary difficulty in making electrochemical measurements of intermetallic compounds found in Al alloys is making them phase pure and of large enough size to work without undue risk of artifact-contaminated measurements. Millimeter-sized phase grains of binary intermetallic phases such as Al_2Cu and Al_3Mg_2 are readily made, but making similarly sized ternary and quaternary phases is exceedingly difficult. We have been able to produce ternary phases such as Al_2CuMg , $\text{Al}_7\text{Cu}_2\text{Fe}$, Al_2CuLi , $\text{Al}_7\text{Cu}_3\text{Li}$ and others with diameters of 100 to 1000 μm . These crystals are too small to mask for electrochemical measurements, but are much larger than the microcapillary cell diameter in the electrochemical microprobe. With the microprobe it is possible easily make replicate measurements on intermetallic compound crystals contained in a single sample. Additionally, it is possible to make measurements on related intermetallic compounds that normally occur in the samples we produce. In this way, trends in electrochemical behavior can be determined. This is very useful in diagnosing mechanisms of localized corrosion.

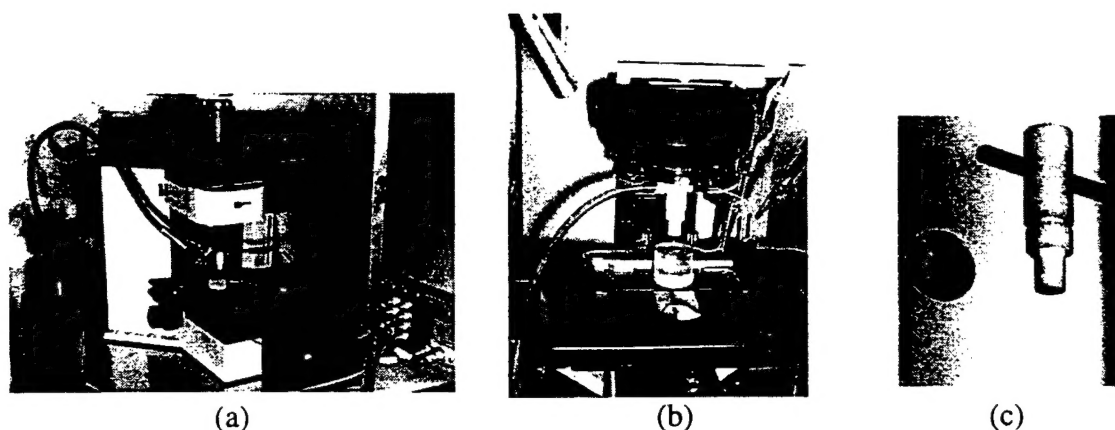


Figure 1. The electrochemical microprobe at Ohio State. (a) The optical microscope situated in a specially constructed Faraday cage. (b) Making a measurement: a close view of a glass capillary contacting a metallographically polished surface. (c) The cell consists of a PTFE solution reservoir containing a Pt wire counter electrode and a bridge to the reference electrode. The drawn glass capillary is affixed to the end of the PTFE reservoir. The entire assembly fits into the objective lens of the microscope.

Scanning Probe Microscope

A Pico scanning probe microscope (SPM) was purchased for imaging corrosion processes and their effects at small length scales using atomic force microscopy and associated imaging techniques. This device is pictured in Figure 2.

Manufacturer's Notes (www.molec.com): Characteristic features of the PicoSPM come from the special design for imaging under controlled conditions. Combination of electrochemistry and environmental control gives the PicoSPM an extreme advantage in the study of solid-liquid interface, either at atomic/molecular resolution or at large scale.

Top-down scanner allows easy access and manipulation of samples. Both STM and AFM scanners can be run by the same microscope. One can easily change scanners from one type to another, thus allowing one to study the same sample with different techniques or change scan ranges within a technique without disassembling the cell. The scanners are completely shielded from chemical vapors so that it can be used with many harsh and volatile solutions.

Magnetic mounting sample plate is easy to mount or dismount, allowing fast exchange of samples. It also leaves the user freedom of modification for running special experiments such as inverted optical spectroscopy and so on. Because the sample remains stationary during imaging, the system shows very low drift.

All Teflon and leak proof cells are easy to assemble and can be acid washed for high-resolution electrochemical experiments. Teflon works very well with almost all liquids, aqueous or non-aqueous. In addition, flow-through system and environmental chambers can be used to reduce contamination and solution loss.

Environmental chambers of variable sizes and functions are able to control the experimental atmosphere, e.g., oxygen level and humidity, by flowing through desired gases.

One can also reduce solvent evaporation when working with volatile solutions by saturating the chamber with solvent. A specially designed dry glove box allows the user to process and load the sample under complete environmental control. This is necessary for experiments involving components sensitive to ambient atmosphere, such as lithiated battery materials. Similarly, one can also use environmental chambers for exposure of samples to hazardous gases.

Heating/cooling stages allow one to study a sample in a wide temperature range from -30 to $+200$ ° C. High resolution, high stability, low noise Bipotentiostat/Galvanostat with easy use and multifunctional software give the user accurate electrochemical control over the electrodes. Simple user programmable script functions allow one to generate complex waveforms. Direct control over the scanning functions is available as well.

32-bit Windows 95, 98, or NT based software comes with the great power of all window's standard features such as multi-window display, easy data sharing, network, and multitask processing. The software, in principle, allows one to open as many as 32 image windows simultaneously. Real-time cross-section display and processing tools add even more power and convenience to (corrosion) research.

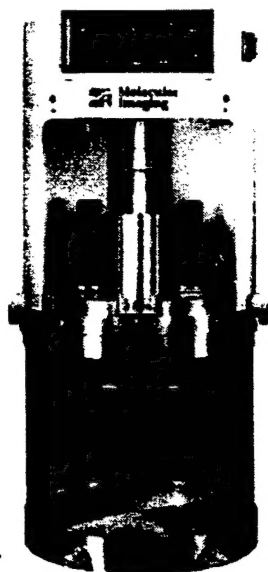


Figure 2. Molecular Imaging's Pico SPM scanning probe microscope.

Rotating Ring Disk Electrode

A Model 636 Rotating Ring Disk Electrode system was purchased from Perkin Elmer Princeton Applied Research Electrochemical Instruments Division. This instrument is capable of operating in either a rotating disk or rotating ring-disk configuration. It is capable of rotational speeds up to 10,000 RPM, and has a quick change electrode capability which is well suited form corrosion studies. This equipment is shown in Figure 3.

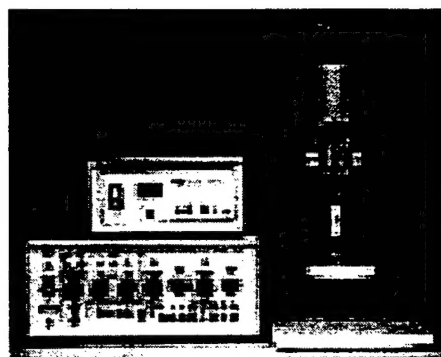
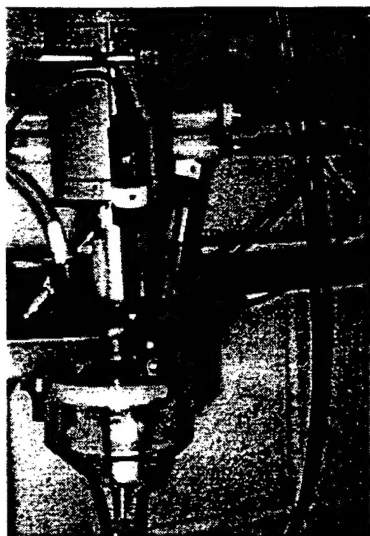


Figure 3. The Model 636 Rotating Ring Disk Electrode system was purchased from Perkin Elmer Princeton Applied Research

Multiplexed Electrochemical Data Acquisition System

Localized corrosion is a stochastic phenomenon and the measured electrochemical parameters that describe it are often distributed. Therefore it is often necessary to make enough experiments to collect sufficiently large populations of measurements to fully describe the parameter distributions. To aid in conducting replicate experiments, an eight channel multiplexed electrochemical work station was purchased. This system in place is a Gamry PC-4 potentiostat combined with a ECM8 Electrochemical Multiplexer. The system was outfitted with software capable of making a variety of measurements including DC corrosion, electrochemical noise, electrochemical impedance, critical pitting potential, and cyclic voltammetry. This system is shown in Figure 4.



Figure 4. The multiplexed electrochemical workstation, and multiple cells under test by the multiplexed workstation.

Multielement Microelectrode Arrays

(From manufacturer's Notes www.sai.com) The Scribner Associates model 900 Multichannel Microelectrode Analyzer (MMA) is designed for use with macro- and micro- scale electrode grids, segmented striplines and other spatial electrode or sensor arrays. Applications include corrosion studies, current distribution analysis, biosensors, chemical sensors, simulated and real crevice monitoring, under film and delamination studies and well as host of novel applications. It has been designed to be a flexible tool for electrochemists wanting to study small, multielectrode systems or sensors.

The model 900 MMA is equipped for up to 100 channels of current measurement with sensitive ZRAs and/or electrode segment potentials with high impedance electrometers. An on-board microprocessor based data acquisition system with 16 bit converters provides wide dynamic range and low noise current and potential measurement. The 100 channels of analog signal conditioning is divided into interchangeable electronics groups of 10 channels each. The signal processing electronics are integrated into the base of the interchangeable test electrode socket for minimum signal path length and optimum shielding.

A built-in potentiostat provides polarization control of the electrode array with a counter electrode and single reference electrode. Offset polarization of an individual electrode segment is possible with a 12 bit D/A for each signal conditioning group. Combination arrays of reference and working electrodes are possible by mixing the signal conditioning group electronics.

The Windows 95/98/NT graphical interface provides for real-time display of electrode currents and/or potentials as a function of spatial position. Different spatial arrangements may be selected, depending on the actual electrode configuration.

A profile of the row and column data may be selected with peak and average values displayed in real time. Data collected by the local microprocessor is updated every 100 milliseconds and presented in the display window. The raw data is logged to files that can be imported into other spreadsheet or graphic display programs, such as Excel or Sigmaplot, for off-line analysis.

Environmental Fracture Systems

To support environmental cracking studies, a constant extension rate load frame was purchased and an alternate immersion tank was constructed. The CERT frame is shown in Figures and the alternate immersion system is shown in Figure 5.

An M-CERT™ constant extension rate test system was obtained from Intercorr International, Inc. The frame is rated for a 44,000 N load capacity, total stroke of 2 inches, and is capable of producing strain rates ranging from 10^{-7} to 10^{-3} s^{-1} .

The system has been modified to conduct aqueous environmental exposures under free corrosion conditions and under potentiostatic or galvanostatic control. The system is currently under use for evaluation of environmental cracking susceptibility for Al-Mg alloys and Al-Li-Cu alloys under development by the Air Force.

Additionally, an alternate immersion (AI) tank was procured to conduct AI exposure of aluminum alloys in accordance with ASTM specifications. This system is shown in Figure 6.

ASTM G 44 "Standard Practice for Evaluating Stress Corrosion Cracking Resistance of Metals and Alloys by Alternate Immersion in 3.5% Sodium Chloride Solution" directs that samples shall be immersed in solution for 10 minutes every hour and emmersed for 50 minutes every hour. Exposures of this type can run for 60 days continuously, or more. This is a very widely used test to screen alloy compositions, heat treatments and processing schedules for their effect on SCC resistance. To properly run such tests an automated system must be used. A special system was constucted since no commercial vendors for this equipment exists. The AI chamber has been in use continuously since its completion in late 1999.

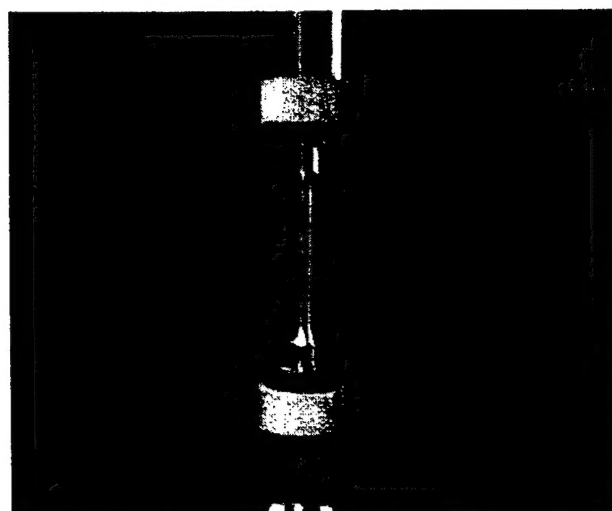


Figure 5. SCC testing of an Al-Mg-Mn alloy in aqueous chloride solutions, and typical round bar sample configuration for constant extension rate testing.

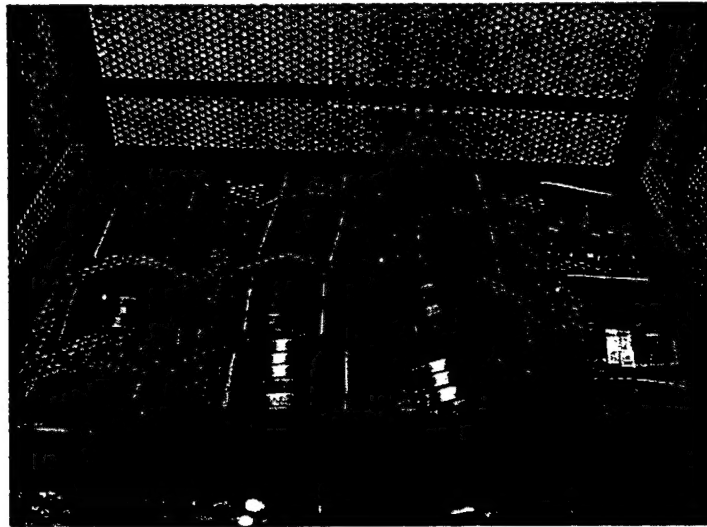
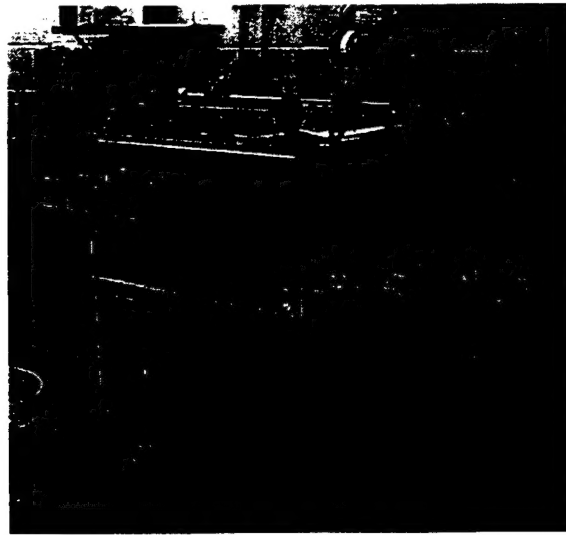


Figure 6. The alternate immersion tank for testing in conformance with ASTM standards for aluminum alloy SCC, and Al-Mg-Mn alloy samples under test in the AI chamber.